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Extensive studies on polymer thin films to date have revealed their interesting but unusual properties such as film thickness dependence of glass transition temperature T_g and thermal expansivity. Recent studies have shown that the lower T_g is not always related to the higher mobility in polymer thin films, which contradicts our current understanding of the glass transition process. In this work, we report the results of inelastic neutron-scattering measurements on polystyrene thin films using two spectrometers with different energy resolutions as well as ellipsometry measurements. The results are interpreted in terms of cooperatively rearranging region and motional slowing down due to the surface effect that explain plausibly the anomalous relationship between the glass transition temperature T_g and the molecular mobility in thin films.

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The state-of-the-art nanotechnology aims to produce functional nanosize devices which require stable, homogeneous, and uniform polymer films in nm scale. This need is driving extensive studies of polymer thin films for more than a decade [1–3]. Such films possess interesting but unusual properties such as anomalous film thickness dependence of glass transition temperature T_g [4–7] and thermal expansivity [8,9]; they also display very large annealing effects and ultraslow relaxation in the molten and glass states [9,10]. Unusual film thickness dependence of glass transition temperature T_g has often been discussed in terms of quasimultilayer structure consisting of, at least, surface mobile layer, middle bulklike, layer and bottom interface layer at a substrate. This quasimultilayer structure has been confirmed in recent fluorescence studies [11] as well as neutron studies [12,13]. It follows that the large annealing effects, including ultraslow relaxation, must be due to residual stress in polymer thin films [10].

Recently, another anomalous property was reported for polymer thin films. As mentioned above, the glass transition temperature T_g decreases with film thickness for polystyrene thin films supported on Si substrate [6]. This property was verified using ellipsometry [4,6] and x-ray and neutron reflectivity [7] in order to determine the glass transition from the measured film thickness as a function of temperature. On the other hand, inelastic neutron scattering (INS) can detect the glass transition temperature T_g from the temperature dependence of a mean-square displacement $\langle u^2 \rangle$, a dynamic property. The result was surprising [14]. The glass transition temperature T_g obtained from INS increases with decreasing film thickness, which is completely contradictory to the ellipsometry, x-ray, and neutron reflectivity results. Furthermore, recent work by Forrest and co-workers on bilayer polystyrene films [15] revealed that as the film thickness decreased the glass transition temperature T_g decreased. At the same time, the time constant for the interface healing process increased. These results suggest that it is not always possible to relate the lower T_g to the higher mobility in the so-called α process. This contradicts our current understanding of the glass transition process.

In order to elucidate this anomaly, we have performed INS measurements on polystyrene thin films using two INS spectrometers with different energy resolutions as well as ellipsometry measurements. The results are discussed in terms of the concept of cooperatively rearranging region (CRR) [16] and motional slowing down due to the surface effect, which provide a plausible explanation of the anomalous relation between the glass transition temperature and the molecular mobility in thin films.

The samples used are atactic polystyrene (aPS) with molecular weight $M_w = 2.9 \times 10^5$ and molecular weight distribution $M_w/M_n = 1.06$, where M_w and M_n are the weight average and the number average of the molecular weight, respectively. The bulk glass transition temperature was estimated by differential scanning calorimetry (DSC) measurement with a cooling rate of 10 °C/min to be 373 K. For the INS studies, aPS thin films were prepared by spin-coating toluene solutions at 2000 rpm on flat glass plates. The thin films were removed from the glass surface onto water surface and then collected on Al foil 15 μm thick and annealed at 413 K for 12 h after drying in vacuum at room temperature for 2 days. For ellipsometry studies, aPS thin films were directly spin coated on Al deposited Si substrates in order to realize similar substrate condition to INS studies; these thin films were annealed under the same condition as the INS samples. INS measurements were performed with an inverted geometry time-of-flight spectrometer OSIRIS with energy resolution δE of about 25 μeV at ISIS (UK) [17] and a neutron backscattering spectrometer HFBS with δE of about 0.80 μeV in National Institute of Standards and Technology (NIST), Gaithersburg [18]. Ellipsometry measurements were performed with spectroscopic ellipsometer (M-2000U, J. A.

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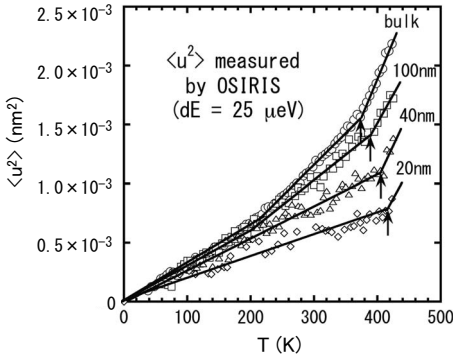

FIG. 1. Temperature dependence of mean-square displacement $\langle u^2 \rangle$ evaluated in INS measurements by OSIRIS with energy resolution of 25 μeV for aPS bulk, 100, 40, and 20 nm films.

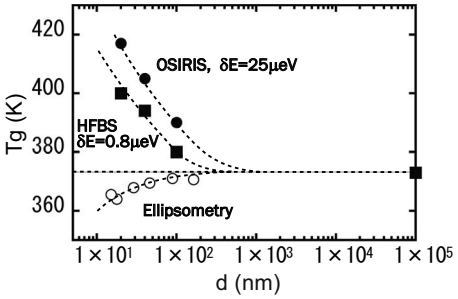

FIG. 2. Glass transition temperatures T_g estimated from temperature dependence of $\langle u^2 \rangle$ measured by OSIRIS and HFBS and T_g estimated from temperature dependence of film thickness measured by ellipsometry.

Woolam, USA). The energy resolutions are approximately related to the time resolutions δt through $\delta t \sim h/\delta E$, where h is Planck constant.

Elastic window scans were performed for aPS bulk, 100, 40, and 20 nm films in a temperature range from ~35 to 425 K using OSIRIS spectrometer. In order to remove the coherent part of the scattering, we have normalized the elastic intensity $I_{el}(Q)$ to that at the lowest temperature (~35 K). Subsequently, we have plotted $I_{el}(Q)/I_{el}(Q)_{lowest}$ against Q^2 in order to evaluate the difference $(\langle u^2 \rangle - \langle u^2 \rangle_{lowest})$ as a function of temperature. Here, $\langle u^2 \rangle$ and $\langle u^2 \rangle_{lowest}$ are the mean-square displacements at some temperature T and the lowest temperature. Q denotes the length of the scattering vector. The evaluated mean-square displacement $\langle u^2 \rangle$ was plotted against temperature for the bulk, 100-, 40-, and 20-nm-thick films in Fig. 1. Note that the data were shifted assuming $\langle u^2 \rangle = 0$ at $T=0$ to correct for $\langle u^2 \rangle_{lowest}$. The $\langle u^2 \rangle$ increases linearly with temperature for the bulk in the low-temperature region, showing that the observed motion is a harmonic vibration. The mean-square displacement then begins to increase slightly steeper above ~200 K, which corresponds to the onset of the so-called picosecond fast process [19]. The slope of $\langle u^2 \rangle$ vs temperature changes again at around 370 K, which is very close to the glass transition temperature T_g(=373K). This implies that the glass transition of aPS could be observed in the measurements. As the film thickness decreases, $\langle u^2 \rangle$ decreases in the whole temperature range examined, showing that the mobility of aPS decreases with the film thickness. Similar thickness dependence was observed in meV region [20,21]. For the 100 nm film, the onset of the fast process was observed at around ~200 K, but not pronounced compared with that observed in the bulk. For the 40 nm films, the onset of the fast process was not observed any more, suggesting that the fraction of the fast process decreases with the film thickness. This agrees with the previous observation in meV region [20,21]. On the other hand, the glass transition temperatures T_g derived from $\langle u^2 \rangle$ were clearly observed for the thin films as shown by up arrows in Fig. 1. These T_g's are plotted in Fig. 2 as a function of film thickness d. It is clear that the T_g increases with decreasing film thickness.

We have also performed ellipsometry measurements on the aPS thin films in order to evaluate the glass transition temperature T_g from the temperature dependence of the film thickness. It is known that a type of substrate affects T_g due to the interaction between the substrate and polymer [5]. Hence, in our measurements aPS thin films were prepared on Al deposited Si substrates to realize similar substrate condition as those in the INS measurements. The deposited Al layer was about 100 nm thick. The evaluated T_g is shown in Fig. 2 as a function of the film thickness. It is evident that as the film thickness decreases T_g from the ellipsometry measurements decreases, while T_g obtained from $\langle u^2 \rangle$ as measured by INS increases. These two dependences of T_g on a film thickness are completely contradictory. As mentioned in the introduction, similar contradiction was reported by Soles *et al.* [14]. They reported for polycarbonate that T_g estimated from $\langle u^2 \rangle$ increased but T_g from thermal expansivity decreased as the film thickness decreased—a qualitative agreement with our observations. This provides an independent confirmation of our results.

There are many factors affecting T_g of polymer thin films such as surface and interface interactions, density, confinement effects, etc. In this paper, we discuss the contradictory thickness dependences of T_g based on the concept of CRR [16] as applied recently by Schönhals *et al.* [22]. They investigated dynamics of glass-forming poly(methyl phenyl siloxane) (PMPS) in nm pores in order to evaluate the temperature dependence of the relaxation time. They used a combination of dielectric spectroscopy, temperature-modulated DSC, and neutron scattering. Bulk PMPS showed the Vogel-Fulcher behavior of the relaxation time for the α process, typical for glass-forming materials. On the other hand, the temperature dependence for PMPS in nm pores gradually changed to the Arrhenius behavior as the pore size decreased.

It is worthwhile to revisit Fig. 6 from Ref. [22]. Note that the relaxation times in various pore sizes merge almost into one point at a certain temperature, which we refer to as a *crossing temperature* T_c or a *crossing point* hereafter. The physical meaning of the crossing temperature T_c will be discussed later. The change in the temperature dependence suggests that the CRR of the segment motion cannot extend even near T_g due to the confinement of nm pore. Furthermore, the apparent activation energy in the Arrhenius behavior decreases with decreasing pore size, suggesting that the CRR size decreases with the pore size. It should be noted

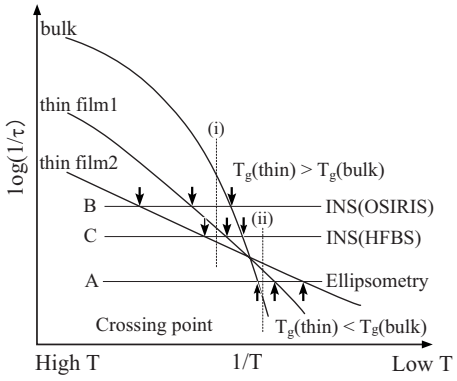

FIG. 3. Schematic sketch of relaxation-time map used to explain the contrary film thickness dependences of T_g in Fig. 2. The map is based on the measurements on PMPS in nm pores [22]. Thin film 2 is thinner than thin film 1.

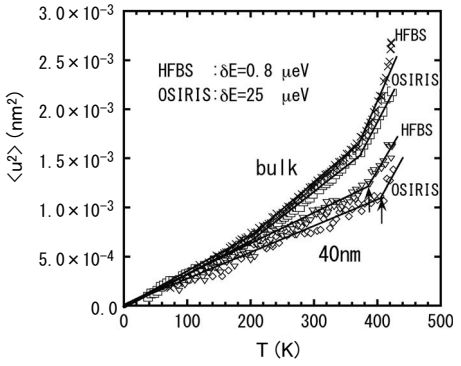

FIG. 4. Temperature dependence of mean-square displacement $\langle u^2 \rangle$ evaluated in INS measurements by OSIRIS and HFBS for aPS bulk and 40 nm film.

that the relaxation time increases with decreasing pore size at high temperatures above the crossing temperature T_c, meaning that the segment motions in a smaller pore are hindered rather more than in a larger nm pore. This slowing down may be caused by the interactions between the segments and the pore surface and/or the effects of a wall of pore. In the latter case, the segment motion is affected by the wall in nm pore, reducing the motional freedom and leading to less mobility [23].

In order to relate our results to those for PMPS, we have constructed a similar relaxation-time map shown in Fig. 3, which serves to explain the conflicting film thickness dependences of T_g derived from the INS and ellipsometry measurements. In the ellipsometry measurements, we evaluate thermal expansivity, which is dominated by the free volume or the α process, meaning that very slow motion dominates T_g in these measurements. For example, assuming that the ellipsometry measurements detect T_g when relaxation time crosses a certain slow characteristic time (line A in Fig. 3), T_g must decrease with the film thickness as shown by up arrows along line A. This agrees with our results. On the other hand, in the INS measurements we observe rather fast motion compared with ellipsometry measurements. Assuming that the OSIRIS spectrometer characteristic time (dominated by the energy resolution δE) lies on line B in Fig. 3, we would observe T_g when the relaxation time crosses line B. Therefore, T_g must increase with decreasing film thickness as shown by down arrows on line B. This again agrees with our neutron-scattering results. Therefore, the relaxation-time map is one of the tools to explain the discrepancy of film thickness dependence of T_g between the ellipsometry and INS measurements.

The concept of a time-scale dependent T_g gives us other predictions. If we perform similar INS measurements but use a spectrometer with higher-energy resolution δE, we should be able to observe slower motions, meaning that we observe the relaxation times along line C in Fig. 3. This predicts that the glass transition temperature T_g decreases as the energy resolution increases. To confirm the prediction, we performed another INS experiments using a backscattering spectrometer HFBS at NIST with higher-energy resolution of 0.8 μeV than that of OSIRIS (25 μeV). The observed temperature dependences of $\langle u^2 \rangle$'s by OSIRIS and HFBS are shown for bulk and 40 nm film as a function of temperature in Fig. 4. Here, the values of $\langle u^2 \rangle$ were shifted to cross $\langle u^2 \rangle = 0$ at $T = 0$ to compare the two measurements. It is evident that the $\langle u^2 \rangle$ is larger in the higher-resolution measurements because the slower motion is observed in the higher-energy resolution measurements. Comparison of $\langle u^2 \rangle$'s for the 40 nm films by HFBS and OSIRIS shows clearly that T_g measured by HFBS have a lower value. The T_g's observed using HFBS are plotted in Fig. 2 as a function of the film thickness. For every film thickness T_g from the HFBS results is lower than that obtained from OSIRIS measurements, confirming the prediction from the relaxation-time map in Fig. 3. It should be noted that T_g in bulk aPS does not differ greatly between the OSIRIS and HFBS measurements. The temperature dependence of the relaxation time in bulk is steep near T_g, and, hence, it is expected that the T_g difference would not be large for the measurements with different energy resolutions.

We can predict yet another feature of thin films from the relaxation-time map in Fig. 3. When we measure relaxation times directly at a given temperature above the crossing temperature T_c as a function of film thickness, for example, along line (i) in Fig. 3, the relaxation time must increase with decreasing film thickness. On the other hand, if measurements are done at a given temperature [say, along a line (ii) in Fig. 3] below the crossing temperature T_c, the relaxation time must decrease with decreasing film thickness. INS measurements using HFBS must be along the line (i) above the crossing temperature because T_g increases with decreasing film thickness. Then, we have analyzed the dynamic scattering laws $S(Q,\omega)$ of the bulk, 100 and 40 nm films at 440 K using a Havriliak-Negami function, and evaluated the relaxation time and the shape parameters [24]. We found that the average relaxation time increased with decreasing film thickness, in agreement with the prediction from the relaxation-time map (Fig. 3). As in this work we have not directly measured the motion of aPS in thin films below the crossing temperature T_c, we have sought an explanation in literature. Fukao and Miyamoto [25] performed dielectric relaxation measurements on aPS films near T_g, which must be below the crossing temperature T_c. They found that peak frequency (or inverse of relaxation time) in the dielectric loss increased

as the film thickness decreased, meaning that the mobility of segments increases with decreasing film thickness. Thus, in the framework of the scenario based on CRR the lower mobility always corresponds to the higher glass transition temperature (cf. Fig. 3). This is physically very sound.

In this work, we have studied T_g and $\langle u^2 \rangle$ of aPS thin films using INS and ellipsometry. It was found that the T_g evaluated from INS increased and the T_g obtained from ellipsometry decreased, respectively, as the film thickness decreased. This contradiction was explained in terms of the relaxation-time map based on the cooperatively rearranging region hypothesis. In this scenario, the lower T_g always means the higher mobility.

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